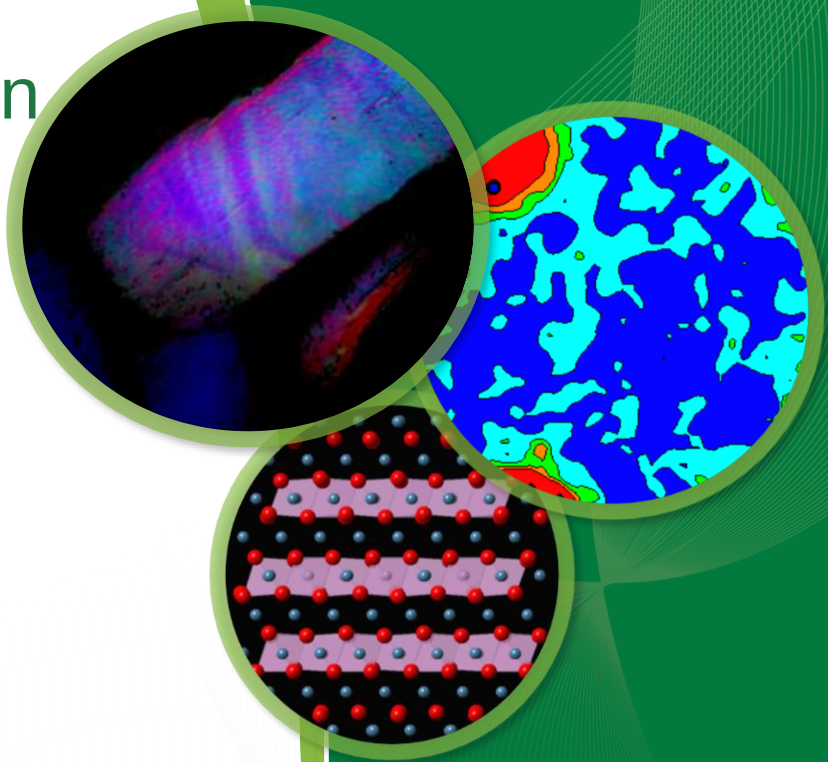
Disordered Rocksalt Transition-Metal Oxides (TMOs): Fluorination Studies and Spectroscopic Characterization



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Oak Ridge National Laboratory

2019 U.S. DOE Vehicle Technologies Office Annual Merit Review

June 12, 2019 **Project ID: BAT404**

ORNL is managed by UT-Battelle
for the US Department of Energy

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Overview

Timeline

- Project start date: Oct. 1, 2018
- Project end date: Sept. 30, 2021
- Percent complete: 30

Budget

- FY19 Funding: $ 400K

Barriers

Performance

Capacity: Cathode specific capacity ≥ 250 mAh/g @ nominal voltage ≥ 3.8 V wrt Li^o/Li^+

Rate: 3C or higher

Life: Minimum 1000 deep discharge cycles

Partners/Collaborators

- Lawrence Berkeley National Laboratory & University of California, Berkeley

Guoying Chen, Wei Tong, Gerd Ceder, Kristin Persson, Bryan McCloskey, Wanli Yang, Robert Kostecki– Synthesis, Modelling & Characterization

- University of California, Santa Barbara
  Raphaële Clément-NMR
- University of Tennessee
  Sheng Dai - Fluorination
- *Pacific Northwest National Laboratory*
  Chongmin Wang- Electron Microscopy

Relevance

Impact

Development of high energy density cobalt-free cathodes are critical to meet the growing demand for advance lithium-ion cell for electric vehicles. In this context, cobalt free high capacity disorder cation rock salt (DRX) is a potential alternative to the layered NMC or NCA based cathode chemistries and can achieve energy densities up to 1000 Wh/Kg

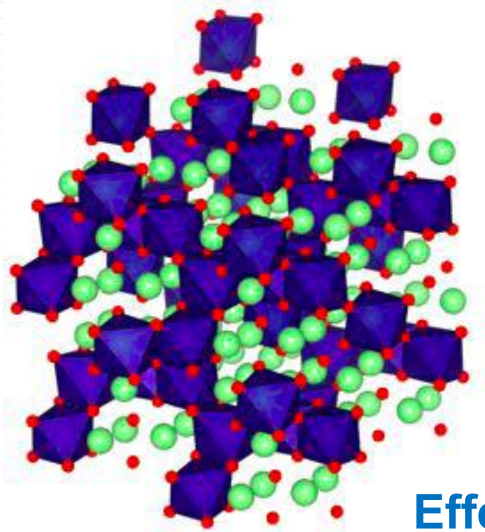
Objectives

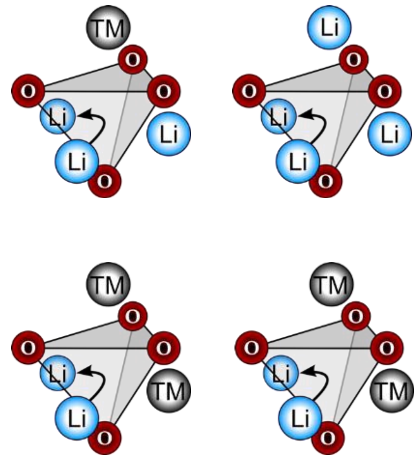
- Synthesis and electrochemical performance optimization of DRX composition based on effective charge compensation
- Undertake alternate fluorination methods for DRX compositions to achieve greater oxidative and cycling stability
- **Characterization** : Use neutron, Raman and NMR methods to understand short-range and long-range structure and correlate with lithium transport

Relevance to VTO Mission

Addressing VTO programmatic goals of understanding and mitigating existing materials issues that prevent *state-of-the-art* Li-ion battery systems from achieving higher practical energy densities, lower cost, safer performance, better lifetimes, and less reliance on security critical materials

Cation disorder rock salt cathodes are a class cobalt free cathodes that provide an effective design framework to achieve high capacity and oxidative stability





Cation disorder rock salt structures allow different Li coordination or bonding environments unlike layered cubic cathodes

At > 10 % Li-excess 0-TM channels form a percolative pathway for lithium diffusion

Effective charge compensation to maximize capacity

- Lower the redox active TM (such as Mn) by high valent substitution – Nb^{5+}, Ti^{4+} Mo^{6+} that are d^0 transition metal configuration
- Lower the anionic charge by replacing O^{2-} with F^{-1}

Composition	TM Cations
$Li_{1+x}V_2O_5$	V^{3+}, V^{5+}
$LiM_{0.5}Ti_{0.5}O_2$ (M = Fe, Ni)	M^{2+}, Ti^{4+}
$Li_{1.211}Mo_{0.467}Cr_{0.3}O_2$	Mo^{5+}, Cr^{3+}
$Li_{1.3}Nb_{0.3+x}M_{0.4-x}O_2$ (M = Mn, Fe, Co, Ni)	Nb^{5+}, M^{3+}
$Li_{1.6-4x}Mo_{0.4-x}Ni_{5x}O_2$	Mo^{6+} Ni^{2+}
$Li_{1.3}Nb_{0.3}V_{0.4}O_2$	Nb^{5+}, V^{3+}
$LiCo_{0.5}Zr_{0.5}O_2$	Co^{2+}, Zr^{4+}

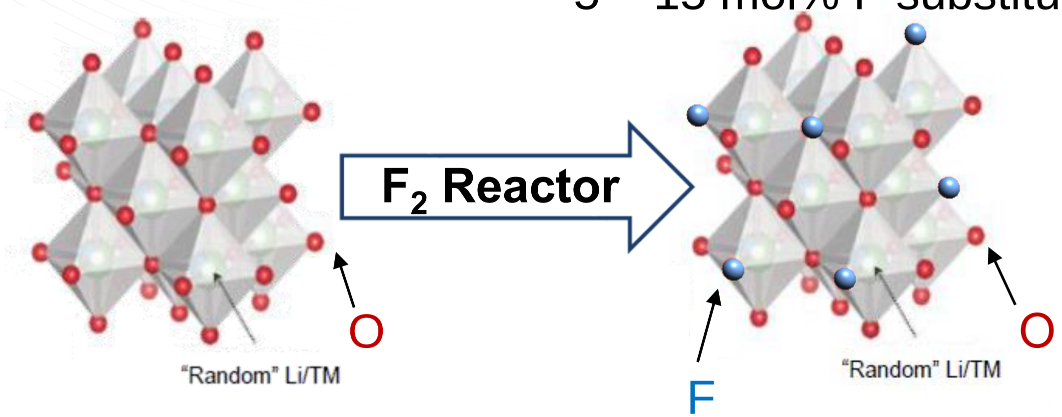
J Lee, et al., Science, 343 (6170), 519-522 (2014)

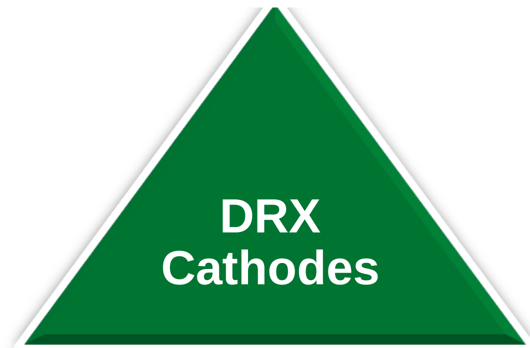
Develop alternate fluorination routes for disorder rock salt (DRX) cathodes other than mechanochemical synthesis

We use an *in-situ* fluorine gas reactor under controlled conditions as one of the strategies to incorporate fluorine in DRX compositions

Baseline DRX Structure

Target: 5 – 15 mol% F substitution





Compositions for investigation at ORNL from DRX deep dive team

- $Li_{1.2}Nb_{0.3}Mn_{0.5}O_2$ (LNMO)
- $Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$ (LMNOF)
- $Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$ (LNTMOF)

Image adapted from: J. Lee et al. *Energy Environ. Sci.* **8**, 3255-3265 (2015).

ORNL Research Scope

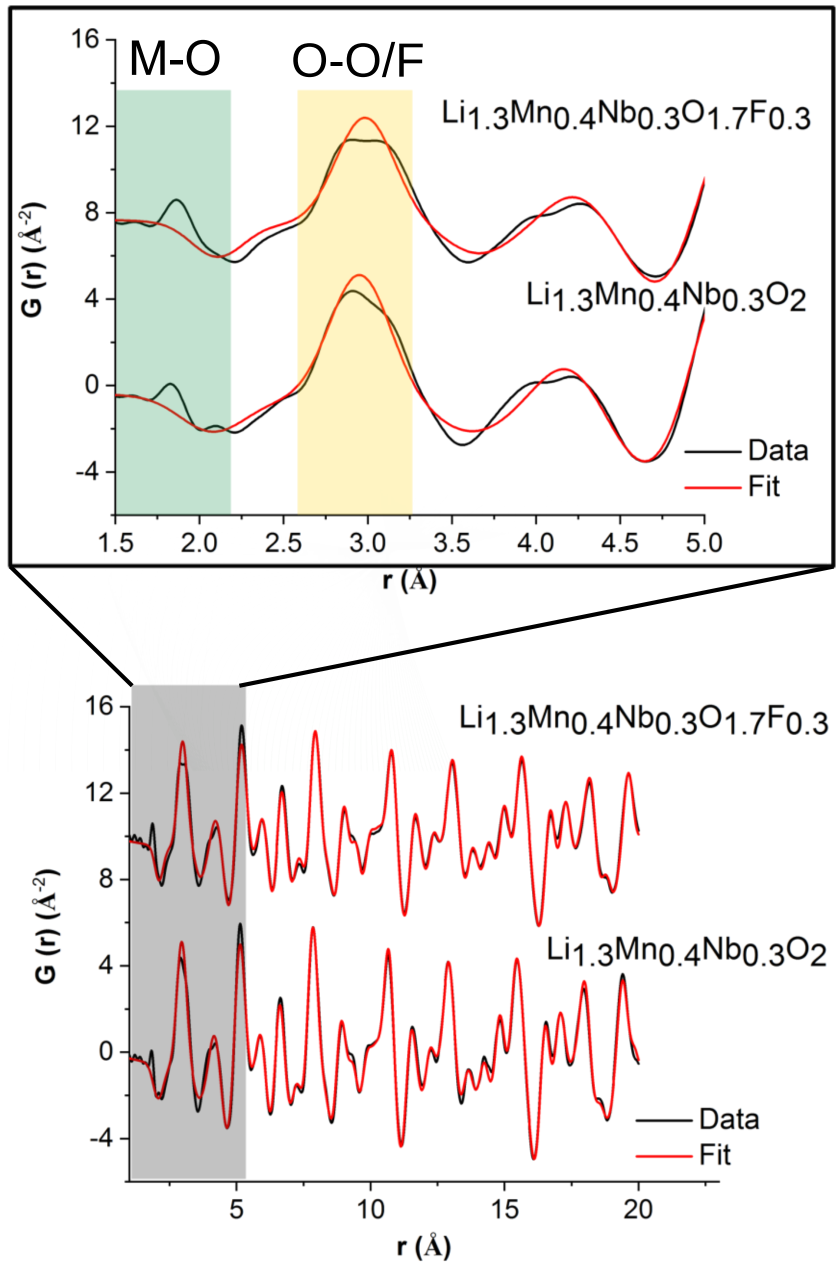
1. Optimize the fluorinated composition for better capacity retention and stability
2. Local structural and spectroscopic characterization of DRX cathodes

Milestones

Due Date	Description	Status
12/31/2018 (Q1)	Complete neutron powder diffraction, microstructural analysis of two DRX compositions – $Li_{1.15}Ni_{0.375}Ti_{0.375}Mo_{0.1}O_2$ and $Li_{1.25}Nb_{0.25}Mn_{0.5}O_2$	Complete
03/31/2019 (Q2)	Undertake fluorination of DRX compositions $Li_{1.15}Ni_{0.375}Ti_{0.375}Mo_{0.1}O_2$ and $Li_{1.25}Nb_{0.25}Mn_{0.5}O_2$ and control the fluorination level between 5-15 %.	Complete
06/30/2019 (Q3)	Complete electrochemical and structural characterization of fluorinated DRX composition and compare with baseline composition (unfluorinated).	In progress
09/30/2019 (Q4)	Develop alternate synthesis method for selected Mn and Ni based DRX cathodes having capacity > 250 mAh/g @ C/10 and nominal voltage > 3.5 V wrt Li^+/Li^o	In progress

Neutron PDF analysis indicates LMNOF cathodes exhibit local short-range ordering (< 5 Å). The local structure changes based on the degree of fluorination.

LMNOF samples from G. Ceder group analyzed at NOMAD (SNS, ORNL)



Long-Range Structure

- Oxide and oxyfluoride DRX compositions exhibit random, disordered Fm-3m structure

Short-Range Structure (< 5 Å)

- Short-range ordering (e.g., O-O peak splitting) deviates from randomly disordered rock-salt structure
- Fluorination changes short-range order

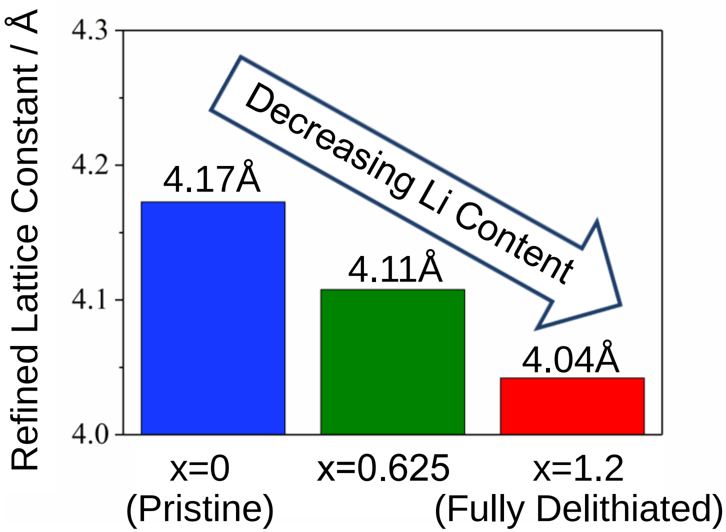
Challenges in Local Structure Determination

- Cation/anion arrangement
- Jahn-Teller distortion from Mn

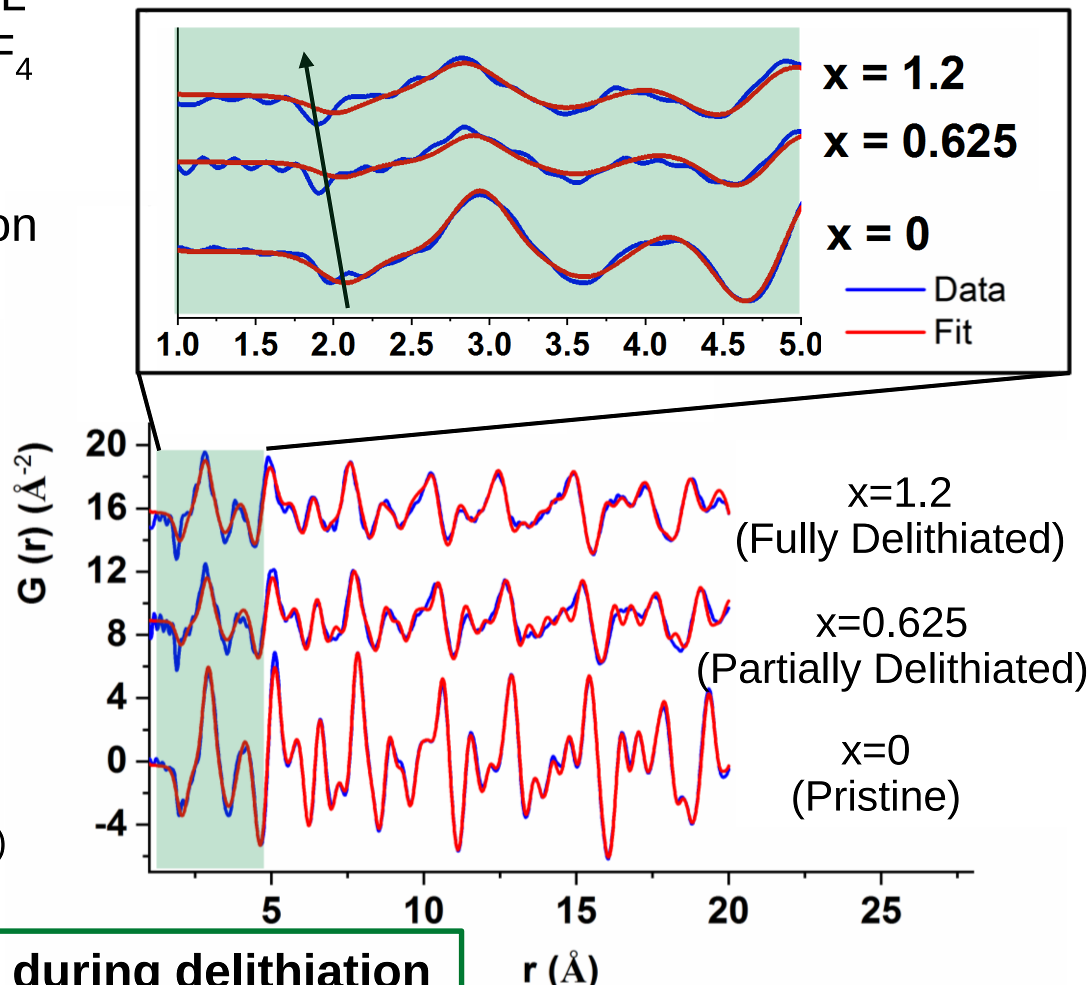
Chemically delithiated LMNOF cathodes show clear changes in the local structure and long-range ordering.

Experimental Details

- LMNOF from Y. Yue, W. Tong, LBNL
- Chemically delithiated using NO_2BF_4 in acetonitrile
  - $Li_{1.2-x}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$
- Local structure probed using neutron PDF (NOMAD)



Neutron PDFs of Delithiated LMNOF



Structural changes which occur during delithiation

(1) Decreased M-O bond length

(2) Loss of long-range ordering

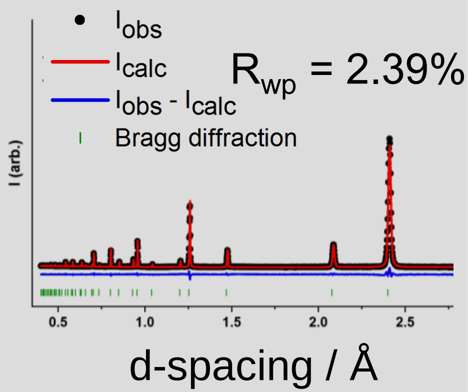
Neutron diffraction was used to determine how cation substitutions (Ti^{4+}, Nb^{5+}) and degree of fluorination affect unit cell parameters of DRX cathodes.

Sample Details

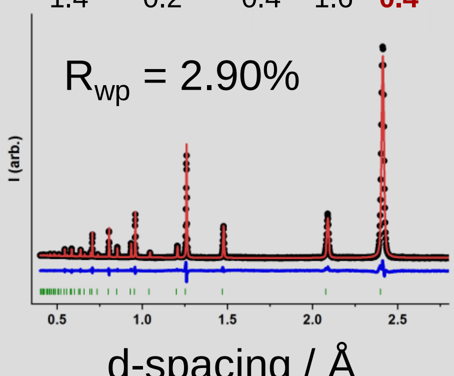
- G. Chen and D. Chen, UC-Berkeley
- Lattice parameters determined from neutron powder diffraction (POWGEN)

Nb^{5+} Substitution

$Li_{1.3}Nb_{0.2}Mn_{0.5}O_{1.8}F_{0.2}$

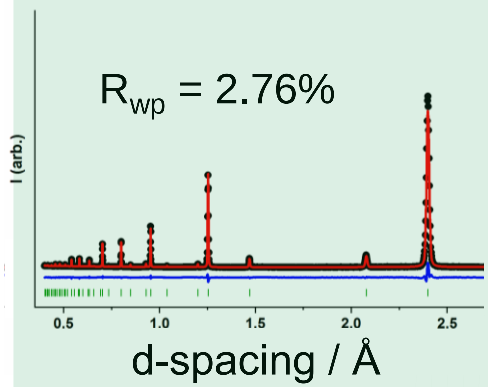


$Li_{1.4}Nb_{0.2}Mn_{0.4}O_{1.6}F_{0.4}$

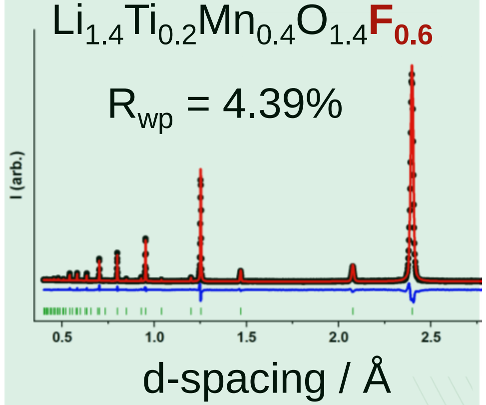


Ti^{4+} Substitution

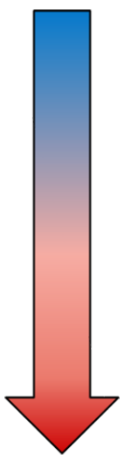
$Li_{1.2}Ti_{0.2}Mn_{0.6}O_{1.8}F_{0.2}$



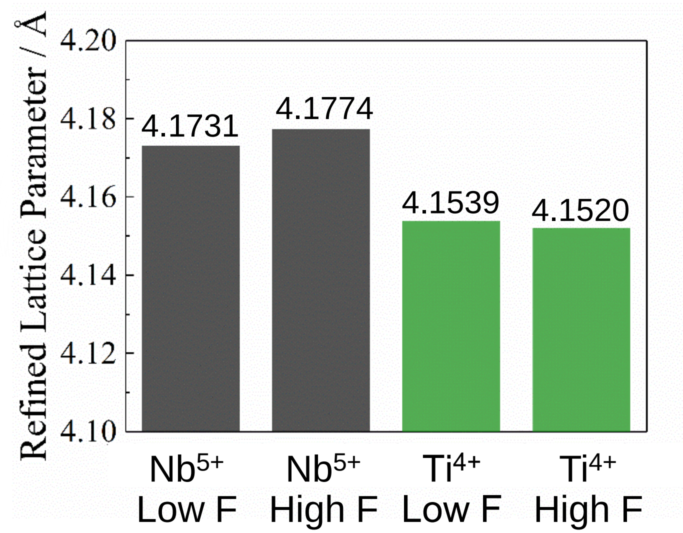
$Li_{1.4}Ti_{0.2}Mn_{0.4}O_{1.4}F_{0.6}$



Low F



High F



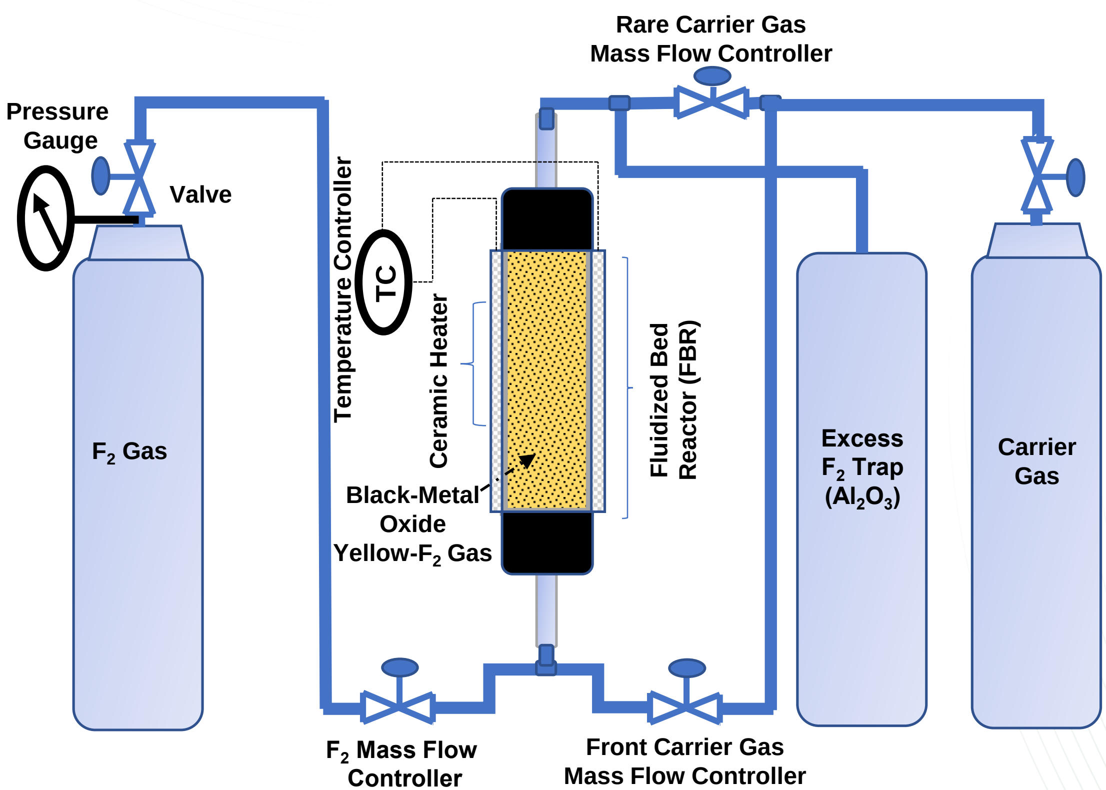
Direct fluorination of DRX cathodes was conducted using exposure to F_2 gas in a fluidized bed reactor.

Samples for fluorination

1. LMNOF ($Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$)
2. LNTMOF ($Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$)
3. LMNO ($Li_{1.3}Nb_{0.3}Mn_{0.4}O_2$)

W. Tong and Y. Yue, LBNL

Dongchang Chen and Guoying Chen, LBNL (LNMO investigations are ongoing)



Fluorination Conditions

Mild

100 °C, 1 h, 1.6 sccm F_2

Moderate

150 °C, 1.5 h, 1.6 sccm F_2

Bishnu Thapaliya & Sheng Dai, UTK

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F_2 reactor conditions (temperature, time) were tuned to control fluorine content in LNTMOF particles.

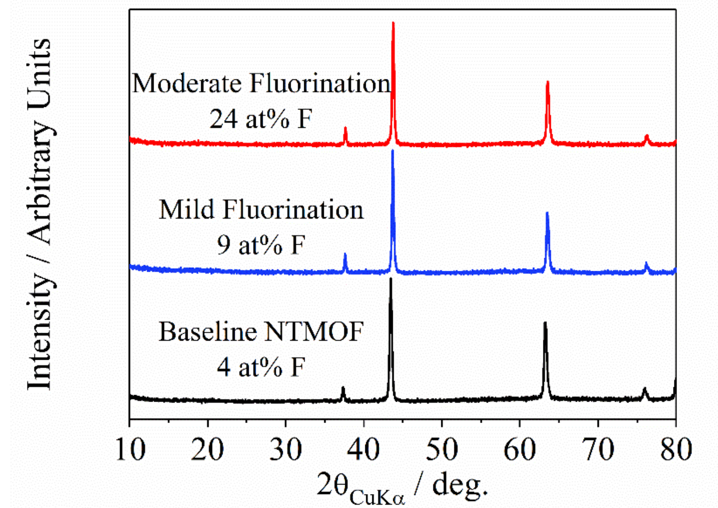
LNTMOF Particles

- $Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$
- Y. Yue and W. Tong, LBNL

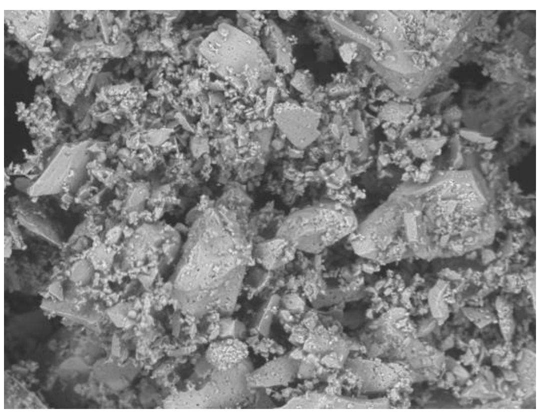
Fluorination Conditions

- **Mild**: 100 °C, 1 h, 1.6 sccm F_2
- **Moderate**: 150 °C, 1.5 h, 1.6 sccm F_2

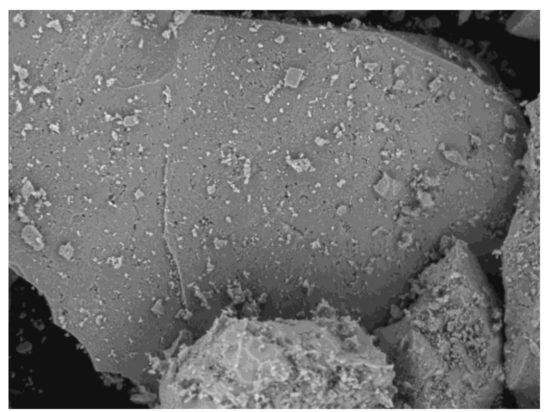
Fluorinated cathodes are phase-pure rocksalt structures.



Unmodified LNTMOF
4 at% F



Mild F_2 Treatment
9 at% F



Moderate F_2 Treatment
24 at% F

100 µm

Increasing Fluorine Content in LNTMOF

Direct fluorination reaction was kinetically less facile for LMNOF compared to LNTMOF. Fluorination of LMNOF did not significantly impact particle size/morphology.

LMNOF Particles

- $Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$
- Y. Yue and W. Tong, LBNL

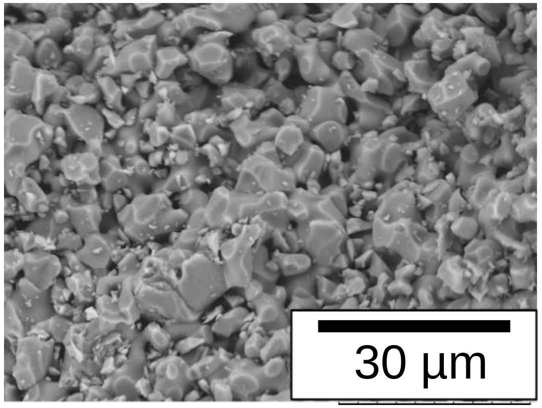
Fluorination Conditions

- **Mild**: 100 °C, 1 h, 1.6 sccm F_2
- **Moderate**: 150 °C, 1.5 h, 1.6 sccm F_2

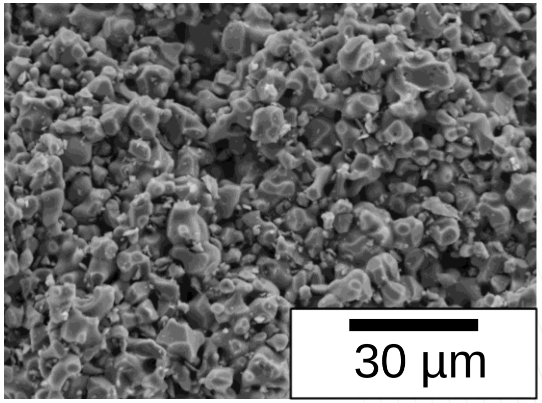
Reaction Condition	Fluorine Content* (at%)	
	LMNOF	LNTMOF
Unmodified	4	4
Mild F_2	6	9
Moderate F_2	8	24

* from EDX analysis of M, O, F signals

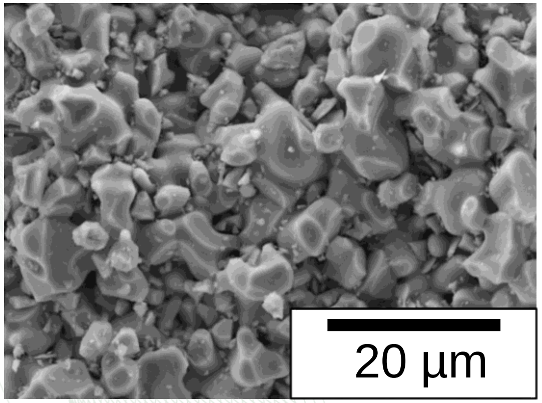
Unmodified LMNOF



Mild Fluorination

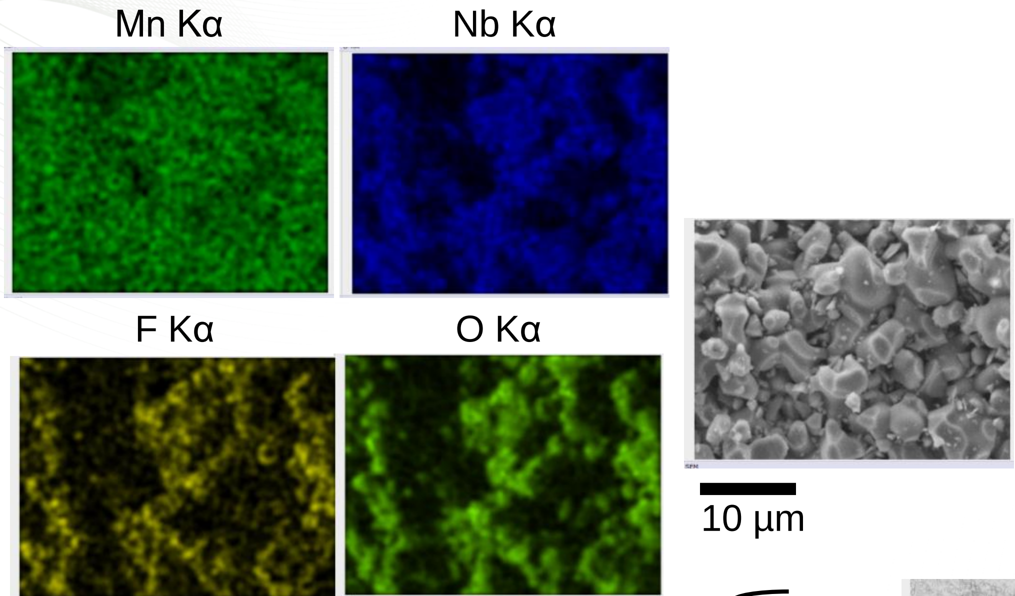


Moderate Fluorination



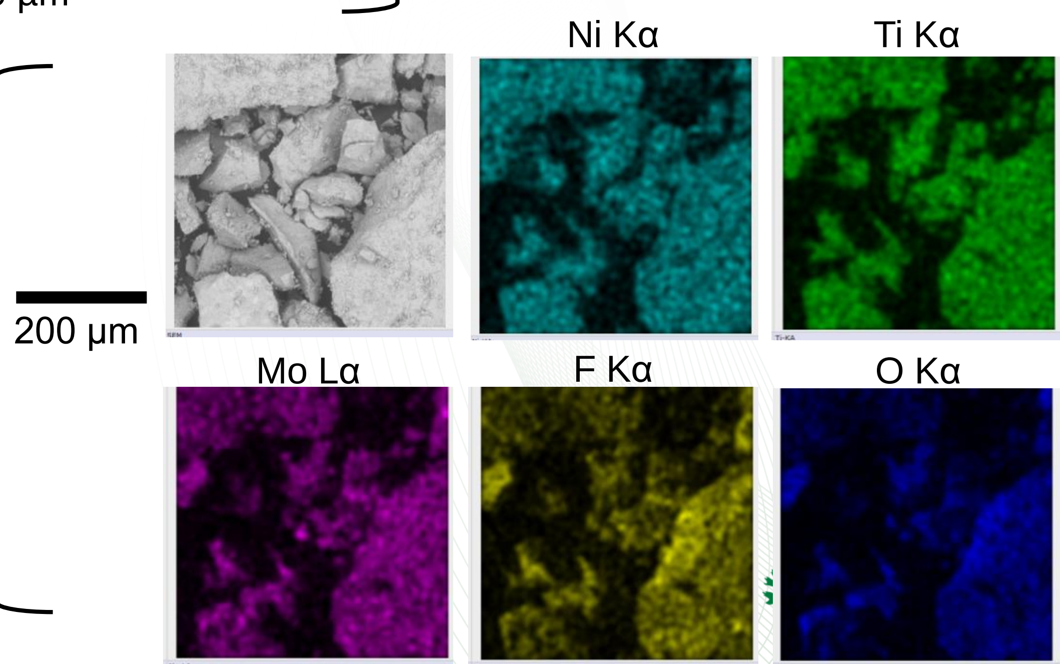
Direct fluorination using F_2 reactor is an viable method to introduce F^- into anion lattice of DRX cathodes.

EDX indicates fluorine content is uniform throughout particle bulk. More detailed structural analysis (e.g., Raman spectroscopy) will be performed after optimal fluorination conditions are identified.



LMNOF after Moderate Fluorination (8 at% F)

LNTMOF after Moderate Fluorination (24 at% F)



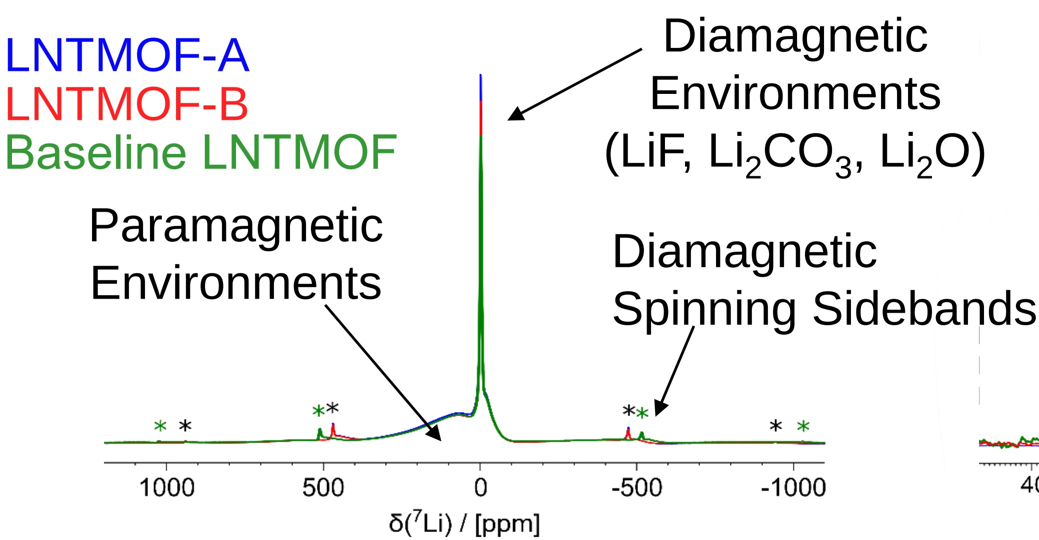
^{7}Li and ^{19}F NMR spectra of LNTMOF cathodes provide valuable insights on how F substitution affects the local chemistry.

^{7}Li and ^{19}F NMR Details

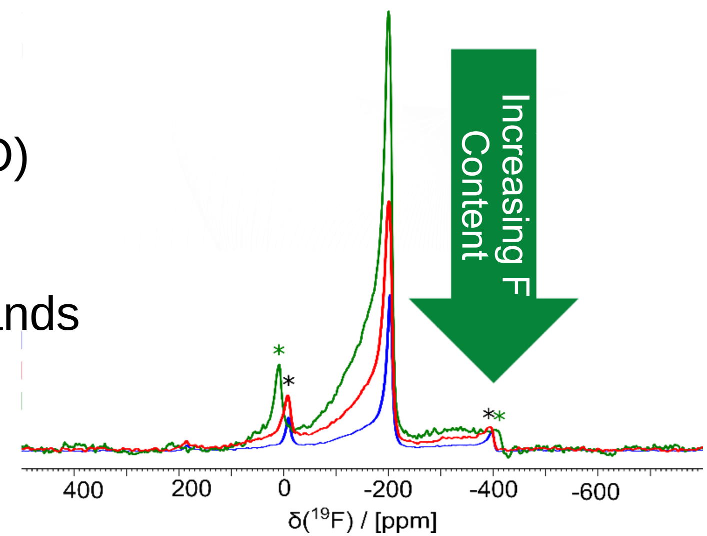
- R. Clément and E. Foley, UCSB
- 55 – 60 kHz
- B_0 = 300 MHz

Sample	F Content (at%)
LNTMOF-A	24
LNTMOF-B	9
Baseline LNTMOF	4

^{7}Li Spin Echo



^{19}F Spin Echo



Key Results and Conclusions

1. Very similar ^{7}Li spectra observed for all samples.
2. Counter-intuitively, larger degree of fluorination decreases ^{19}F signal intensity.
3. Direct fluorination of NTMOF forms paramagnetic domains (e.g., NiF_2).

Response to Reviewers Comments

New project started in FY 19 : Not reviewed

Collaborations and Coordination with DRX deep dive members

DRX Cathode Synthesis and Modelling
Guoying Chen, Wei Tong, Gerd Ceder, Kristin Persson

Bryan McCloskey (**DEMS**)
Wanli Yang (**ALS- RIXS**)
Robert Kostecki (**Interfaces**)

NMR Studies on DRX
Raphaële Clément

Electron Microscopy
Chongmin Wang

Fluorination Studies
Sheng Dai

Neutron Characterization
Jue Liu

Remaining Barriers and Challenges

- Batch sizes for typical DRX cathodes are ~1 - 2 g. Scaling up to larger batches (5 - 10 g) would enable more extensive experimental designs for direct fluorination and electrochemical testing.
- Models must be developed to determine short-range (< 5 Å) cation/anion ordering in DRX cathodes. These models should account for phenomena such as charge shielding and Jahn-Teller distortions.
- Direct fluorination may result in formation of nanocrystalline and/or amorphous domains (e.g., NiF_2) which are difficult to analyze via diffraction.
- Some DRX cathode compositions have very large primary particles (e.g., 50+ µm for $Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$) which may limit cell power density. Alternate synthesis routes and processing methods should be identified to reduce particle size.

Any proposed future work is subject to change based on funding levels

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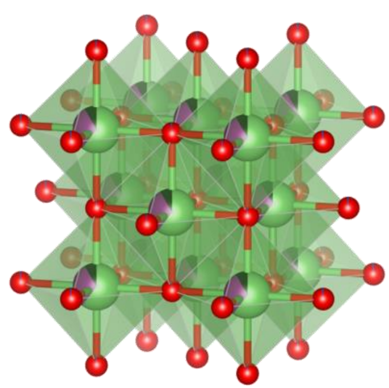
Proposed Future Research

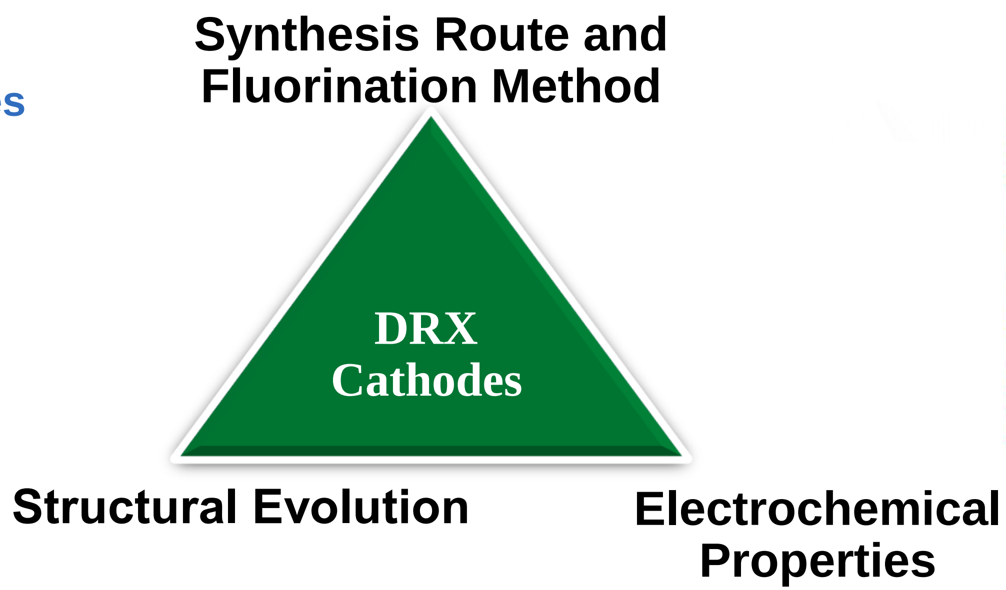
1. Construct and test half-cells containing a DRX cathode, Li metal anode, and carbonate liquid electrolyte. Establish structure/performance correlations to understand how the fluorination method (direct vs. mechanochemical) and fluorine content affect the cathodes' electrochemical properties.

2. Perform *in-situ* Raman spectroscopic studies on DRX cathodes to evaluate any structural changes which may occur during cycling. Combine these results with neutron scattering and NMR studies to determine how F substitution affects the cathode structure and local bonding environments.

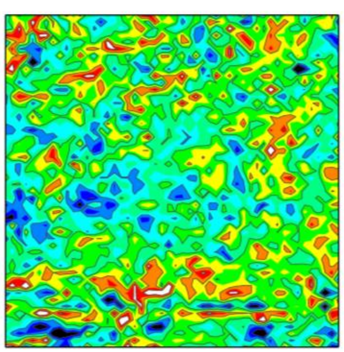
3. Develop alternate synthesis strategies to produce DRX cathodes. Methods to be explored include sol-gel, hydrothermal, and co-precipitation routes. Follow-on experiments will investigate whether the optimal fluorine content depends on the DRX synthesis route.

Fluorinated DRX Cathodes





Raman Mapping

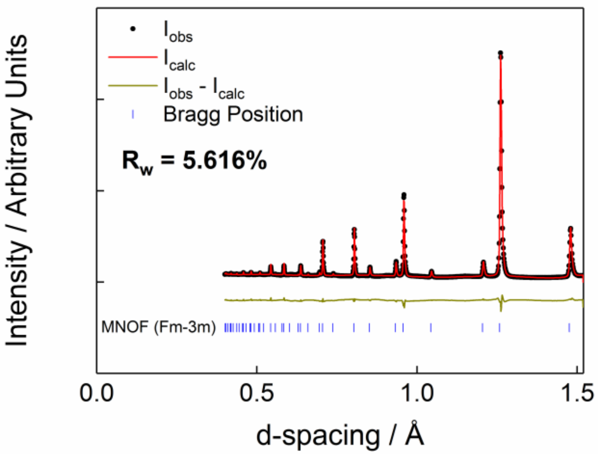


Summary

Technical Approach:

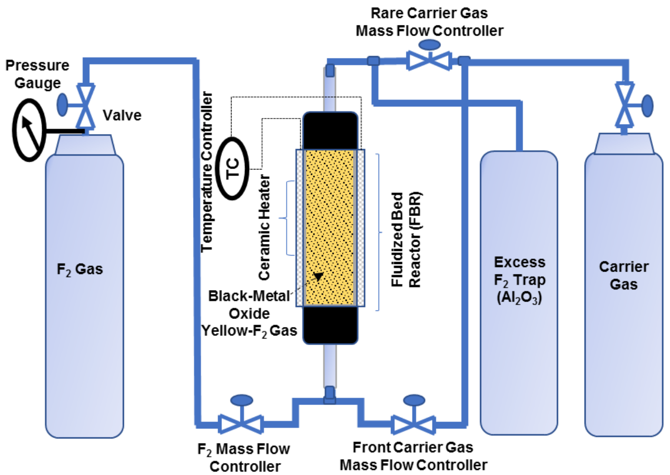
Substitute F^- into anion lattice of disordered rocksalt (DRX) cathodes using F_2 reactor

- Emphasis is placed on understanding how F substitution affects DRX structure and electrochemical performance
- Diagnostic tools include a neutron scattering, microscopy, and vibrational spectroscopy



Accomplishments:

- Identified F_2 reactor conditions to control fluorination level at ca. 5 – 25 at% for LNMOF and LNTMOF cathodes
- Assessed local chemistry and bonding environments of fluorinated DRX cathodes using ^7Li and ^{19}F NMR
- Investigated long-range vs. short-range (< 5 Å) structure of several DRX compounds using neutron scattering.



Ongoing work:

- Optimize F_2 reactor conditions for LNMOF and LNTMOF cathodes
- Develop model to describe short-range cation/anion ordering in DRX cathodes
- Evaluate electrochemical performance of oxide vs. oxyfluoride DRX cathodes